COMPUTATION OF HEAT CAPACITIES OF SOLID STATE BENZENE, p-OLIGOPHENYLENES AND POLY-p-PHENYLENE

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Abstract

Heat capacities \((C_p)\) of solid benzene, biphenyl, \(p\)-terphenyl, \(p\)-quaterphenyl, and poly-\(p\)-phenylene were analyzed using the ATHAS Scheme of computation. The calculated heat capacities based on approximate vibrational spectra of solid benzene and the series of oligomers containing additional phenylene groups were compared to experimental data newly measured and from the literature to identify possible additional large-amplitude motion. The skeletal heat capacity was fitted to the Tarasov equation to obtain the one- and three-dimensional vibration frequencies \(\Theta_1\) and \(\Theta_3\) using a new optimization approach. Their relationship to the number of phenylene groups \(n\) is: \(\Theta_1 = 426.0 - 150.3/n\); and \(\Theta_3 = 55.4 + 81.8/n\). Except for benzene, the quantitative thermal analyses do not show significant contributions from large-amplitude motion below the melting temperatures.

Keywords: benzene, biphenyl, heat capacity, poly-\(p\)-phenylene, \(p\)-quaterphenyl, \(p\)-terphenyl

Introduction

Using the ATHAS, the Advanced Thermal Analysis System, a data bank has been collected with information on thermodynamic properties of currently nearly 250 linear macro-molecules and small molecules [1]. Recently, heat capacities of the solid states, mesophases, and liquids were collected for two series of oligomers of increasing chain lengths. The first consisted of paraffins up to polyethylene [2], the second of perfluoroparaffins leading to polytetrafluoroethylene [3]. It was found that the same group vibrations could be used to compute the heat capacities of oligomers and polymers, and the skeletal vibrations could be represented for molecules of more than a few atoms by simple functions of the chain length, \(n\). For the paraffins and polyethylene a gradual increase in heat capacity beyond that of the vibrational contribution was found below the melting temperature. This increase in \(C_p\) could be attributed to large-amplitude motion, leading to a small amount of conformational disorder [2]. The perfluoroparaffins, in contrast, gain most of their conformational disorder in first-order transitions far below ultimate melting (isotropization) [3]. The behavior of phenylene groups is quite different from the smaller and more flexible \(CH_2\) groups. The connecting bonds between phenylene
groups have a bond angle of 180°, i.e. there is no deflection of the chain on rotation (no flexibility). In fact poly-p-phenylene is not a flexible polymer and decomposes at about 800 K before melting. Rotation of the phenylene groups about their backbone axis is, however, possible and the special effect this causes for the heat capacity is discussed.

In the present paper the connection between measured and calculated heat capacities of solid state of a homologous series of p-oligomers containing phenylene groups is estimated using the ATHAS computation scheme. The calculation of the heat capacities of solids have been made using data from literature on benzene [4], p-biphenyl, p-terphenyl, p-quaterphenyl [5-11], poly-p-phenylene [1] and also from new measurements from our laboratory [12]. The calculations are based on approximate vibrational spectra for the group vibrations and on skeletal spectra obtained by fitting the experimental heat capacities to the Tarasov equation [13]. The parameters Θ_1 and Θ_3 of the Tarasov equation were found using a new optimization approach [14, 15]. The agreement between calculated and experimented heat capacities is, as usual, better than ±3%. Except for benzene, the analyzed materials can be treated as a homologous series with Θ_1 and Θ_3 changing predictably with the molecular size. Further improvement of the Tarasov equation for ring structures are under consideration [12].

**Calculation of the heat capacity for the solids**

The computations of heat capacities for solids are based on the ATHAS scheme [16]. First, the low-temperature experimental heat capacities at constant pressure C_p(exp) from 5-300 K are converted to heat capacities at constant volume C_v using the Nernst-Lindemann approximation [17, 18]. The experimental heat capacities C_v(exp) can, next, be separated into contributions from the group vibration C_v(gr) and from the skeletal vibrations C_v(sk). The contribution C_v(gr) is computed using frequencies obtained from normal mode calculations fitted to results from infrared and Raman spectroscopy. After subtracting the heat capacity contributions of the group vibrations from the experimental C_v(exp), C_v(sk) remains. The C_v(sk) is then fitted to the Tarasov function at sufficiently low temperatures to obtain the two characteristic temperatures (frequencies) Θ_1 and Θ_3. The temperature Θ_1 represents the upper frequency limit of the intramolecular vibrations, Θ_3, the upper frequency limit of the intermolecular vibrations.

Once Θ_1 and Θ_3 are established, a heat capacity that corresponds only to the vibrational motion can be calculated with confidence for any temperature. In reverse, the calculated C_v(sk) is added to C_v(gr) to give the total heat capacity C_v(tot). By conversion to constant pressure, C_p(tot) is obtained for comparison with C_p(exp).

For each member of the series of p-oligomers the number of normal modes of vibration is 3N. These were separated into group vibrations (N_gr) and skeletal vibrations (N_sk) based on the chemical structure. For example, solid benzene with N=12 atoms has 36 normal modes of vibrations, which split into 30 group vibrations and 6 skeletal vibrations (3 of translational and 3 of rotational types of the molecule as a whole) [19]. For the other members of the p-oligophenyls, each ad-